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(54) Polymer-supported catalysts

(57) A supported catalyst comprises (a) a support comprising (i) an insoluble polymer for example polypropylene and (ii) side chains grafted to the backbone of the polymer and (b) a catalyst compound containing a transition metal, chemically bonded to the side chains. The side chains preferably comprise alkene residues and contain a suitable site to which the catalyst compound can be bonded. Suitable alkenes include 4-vinyl pyridine and p-styryldiphenylphosphine. Suitable catalyst compounds include dicobalt octacarbonyl and hydridocarbonyltris(triphenylphosphine)rhodium(I). Supported catalysts of the present invention are suitable for hydroformylation of alkenes.

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SPECIFICATION

Supported catalysts

The present invention relates to supported catalysts.

A supported catalyst is one in which the catalyst sites are attached to an insoluble substrate for example a synthetic polymer. A supported catalyst has the advantage of having a chemistry similar to that of an analogous homogeneous catalyst whilst being capable of removal by filtration methods like a heterogeneous catalyst.

It is an object of the present invention to provide a supported catalyst of improved specificity and selectivity.

According to a first aspect of the present invention a supported catalyst comprises (a) a support comprising (i) an insoluble polymer and (ii) side chains grafted to the backbone of the polymer, and (b) a catalyst compound, containing a transition metal, chemically bonded to the side chains. Preferably the polymer is not significantly affected by high energy radiation. Polymers which are significantly cross-linked, or degraded or have their structures altered in any way by high energy radiation are unsuitable as polymer supports.

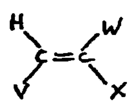
A polymer selected from the polyolefins or from the nylons may be employed as the polymer backbone of the support. It is preferred that the polymer backbone of the support is polypropylene.

Examples of catalyst compounds include cobalt carbonyl and hydridocarbonyltris(triphenylphosphine)rhodium(I).

According to a second aspect of the present invention a method of producing a supported catalyst includes the steps of (a) irradiating a mixture of a polymer and a co-reactant with high energy radiation to produce a polymer support and (b) chemically bonding a catalyst compound to the co-reactant. Step (b) may be performed prior to step (a) but it is preferred that step (a) is carried out before step (b).

Advantageously the high energy radiation is provided in the form of gamma-radiation for example emitted by a ^{60}CO source, although high energy electrons, ultra-violet radiation or X-rays of a suitable wavelength may also be used to provide sufficient energy to carry out the free radical addition reaction.

Preferably the co-reactant is an alkene having the following molecular structure:



.....Formula I

where X is a substituent carrying a suitable group containing a site to which the catalyst compound may be attached. Such a site may be an amine if the catalyst compound includes cobalt, tertiary phosphine, or tertiary arsine if the catalyst compound includes rhodium.

V and W both may be alkyl groups or both H or one may be an alkyl group whilst the other is H. If V and W are both alkyl groups they may be the same alkyl group or they may be different alkyl groups.

Examples of suitable alkenes of the structure shown in formula I include 4-vinylpyridine and p-styryldiphenylphosphine.

The catalyst compound may be attached to the group X of the alkene prior to reacting the alkene with the polymer but is is preferred that the alkene is reacted with the polymer before attaching the transition metal compound to the group X.

Preferably step (a) of the second aspect is carried out in a solvent which is unaffected by gamma-radiation at the given total dose. Suitable solvents include aromatic hydrocarbons such as benzene and toluene, dioxan, dimethylsulphoxide, dimethylformamide and alcohols. Additives such as radical inhibitors which affect the gamma-radiation grafting of alkenes onto polymers may also be incorporated in the reaction mixture. Examples of such additives are p-*tert*-butylcatechol, mineral acids and other suitable substances which may provide H^+ in the reaction mixture.

It will be clearly apparent to those skilled in the grafting art that the reaction undergone in step (a) of the second aspect may be controlled to achieve the desired degree of grafting by altering any one or more of the following variables:

i total irradiation dose;
ii dose rate;
iii the ratio of polymer to alkene;
iv solvent;
v the additives incorporated in the reaction mixture.

Advantageously the polymer is in the form of a powder before the grafting reaction is carried out.

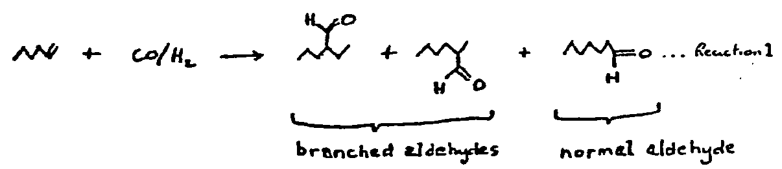
The resultant of step (a) of the second aspect is a graft copolymer, comprising a polymer backbone to which are bonded short chains derived from the polymerisation of the alkene. The grafting of the side chains occurs either on the polymer surface or in the amorphous regions of the polymer.

The catalyst compound may be conveniently attached to the side chains by ligand exchange or ligand replacement reactions.

The microenvironment created by the gamma-radiation grafted alkene side chains modifies the specificity and selectivity of the catalytic sites and also hinders the metal compound from leaching off the support.

According to a third aspect of the present invention a method of carrying out a catalytic organic reaction includes carrying out the reaction in the presence of the supported catalyst of the first aspect prepared according to the second aspect.

It has been found that the support catalysts of the present invention may be advantageously used in the hydroformylation of alkenes which may be represented by the following reaction:



where  represents an alkene.

The improved specificity of the supported catalyst of the first aspect of the present invention ensures that high yields of the normal aldehydes as shown in reaction 1 are obtained whereas only low yields of the branched aldehydes are obtained. A higher normal aldehyde to branched aldehyde ratio is achieved with the supported catalysts of the present invention than is achieved with analogous homogeneous catalysts or other heterogeneous catalysts, under analagous conditions.

The improved selectivity of the supported catalyst of the first aspect of the present invention is demonstrated by the effectiveness of the catalyst to promote hydroformylation of 1-hexene but not the hydroformylation of either *cis* or *trans*-2-hexene in the presence of 1-hexene. This is in part responsible for the enhanced ratio of normal to branched aldehydes produced.

A high normal aldehyde yield is advantageous because the normal aldehydes are commercially important materials which are used for example in the manufacture of plasticisers.

Branched aldehydes are an undesirable by-produce which cannot be used in the manufacture of plasticisers and are therefore either recycled or burnt for energy both of which are expensive and wasteful. By using the supported catalysts of the present invention in the hydroformylation of alkenes such wasteful by-products are greatly reduced.

Embodiments of the present invention will now be described by way of example.

Example 1. A polymer, polypropylene, was suspended in benzene and 4-vinylpyridine added, the whole then being deoxygenated by freeze-degassing and then kept under nitrogen. The appropriate additive p-*tert*-butylcatechol was included before de-oxygenation. The reaction mixture was stirred under nitrogen and γ-irradiated until the appropriate total dose (2 Mrad) had been given at a dose rate of 300 Krad hour^{-1}. After irradiation the polymer powder was removed by filtration and soxhlet extracted with benzene/chloroform followed by methanol to remove any unreacted alkene and any homopolymer formed by the alkene. The product was removed by filtration and dried *in vacuo* to give the polymer support.

The polymer support was reacted at 180°C *in situ* in an autoclave with dicobalt octacarbonyl $(Co_2(CO)_8]$ together with hex-1-ene and a 1:1 mixture of hydrogen and carbon monoxide in benzene solvent at an initial pressure of 100 atmospheres at 20°C. Under these conditions the cobalt reacted with the pyridine sites and modified the system such that the normal to branched ratio was increased to more than twice the value obtained if docobalt octacarbonyl was used without the support. This latter homogeneous system does not give a significantly higher ratio if either pyridine or polypropylene powder alone is added.

Example 2. A polymer support was formed in a similar way to that described in Example 1 using the alkene p-styryl diphenylphosphine. This was then stirred in suspension in a solution of hydridocarbonyltris(triphenylphosphine)rhodium(I) causing an exchange reaction to occur between the triphenylphosphine initially coordinated to rhodium and the polymer supported phosphines. In this way the rhodium complex was attached to the polymer.

The polymer supported catalyst was introduced into an autoclave together with hex-1-ene and a 1:1 mixture of hydrogen and carbon monoxide in benzene solvent and the reaction performed at 10 atmospheres and 60°C. The normal to branched ratio of the products was nearly twice that obtained with the homogeneous analogue hydridocarbonyltris(triphenylphosphine)rhodium(I).

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CLAIMS

1. A supported catalyst including (a) a support comprising (i) an insoluble polymer and (ii) side chains grafted to the backbone of the polymer and (b) a catalyst compound containing a transition metal, chemically bonded to the side chains.

2. A supported catalyst as claimed in claim 1 and wherein the polymer is essentially unaffected by high energy radiation at a given total does.

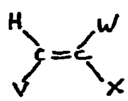
3. A supported catalyst as claimed in claim 1 or claim 2 and wherein the polymer is a polyolefin or a nylon.

4. A supported catalyst as claimed in claim 3 and wherein the polymer is polypropylene.

5. A supported catalyst as claimed in any one preceding claim and wherein the catalyst compound is an organic cobalt compound or an organic rhodium compound.

6. A supported catalyst as claimed in claim 5 and wherein the catalyst compound is dicobalt octacarbonyl or hydridocarbonyltris(triphenylphosphine)rhodium(I).

7. A supported catalyst as claimed in any one preceding claim and wherein the side chains grafted to the backbone of the polymer of the support comprise the residues of alkenes of general formula



..... Formula I

where X is a substituent carrying a suitable group containing a site to which the catalyst compound may be bonded, V and W are alkyl groups or H, and which substituents V and W may be the same or different.

8. A supported catalyst as claimed in claim 7 and wherein the substituent X contains an amine when the catalyst compound is a cobalt compound.

9. A supported catalyst as claimed in claim 7 and wherein the substituent X contains tertiary phosphine or tertiary arsine when the catalyst compound is a rhodium compound.

10. A supported catalyst as claimed in claim 8 and wherein the alkene of which the side chains comprise is 4-vinyl pyridine.

11. A supported catalyst as claimed in claim 9 and wherein the alkene of which the side chains comprise is p-styryldiphenylphosphine.

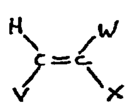
12. A method of producing a supported catalyst as claimed in claim 1 includes the steps of (a) irradiating a mixture of a polymer and a co-reactant with high energy radiation to produce a polymer support and (b) chemically bonding a catalyst compound to the co-reactant.

13. A method as claimed in claim 12 and wherein step (a) is carried out prior to step (b).

14. A method as claimed in claim 12 or claim 13 and wherein the high energy radiation is in the form of gamma-radiation, high energy electrons, ultra-violet radiation or X-rays.

15. A method as claimed in claim 14 and wherein the high energy radiation is in the form of gamma-radiation provided by a ^{60}Co source.

16. A method as claimed in any one of claims 12 to 14 and wherein the co-reactant is an alkene having a general formula



..... Formula I

where X is a substituent carrying a suitable group containing a site to which the catalyst compound may be bonded, V and W are alkyl groups or H and which substituents V and W may be the same or different.

17. A method as claimed in claim 16 and wherein the substituent X contains an amine, tertiary phosphine or tertiary arsine.

18. A method as claimed in claim 17 and wherein the alkene is 4-vinylpyridine.

19. A method as claimed in claim 17 and wherein the alkene is p-styryldiphenylphosphine.

20. A method as claimed in any one of claims 12 to 19 and wherein step (a) is carried out in a solvent which is unaffected by gamma-radiation at a given total dose.

21. A method as claimed in claim 20 and wherein the solvent is an aromatic hydrocarbon, dioxan, dimethylsulphoxide, dimethylformamide or an alcohol.

22. A method as claimed in claim 21 and wherein the solvent is benzene.

23. A method as claimed in any one of claims 12 to 22 and wherein the polymer of the support is in the form of a powder prior to grafting of the side chains to the backbone of the polymer.

24. A method as claimed in any one of claims 12 to 23 and wherein the catalyst compound is chemically bonded to the side chains of the support by ligand exchange or ligand replacement reaction.

25. A method as claimed in any one of claims 12 to 24 and wherein the compound is chemically bonded to the polymer support in situ in an organic reaction mixture for which the presence of the supported catalyst is necessary for the organic reaction to proceed.

26. A method of producing a supported catalyst as claimed in any one of claims 12 to 25 and substantially as hereinbefore described with reference to the Examples.

27. A method of carrying out a catalytic organic reaction including carrying out the reaction in the presence of a supported catalyst as claimed in any one of claims 1 to 11 and substantially as hereinbefore described with reference to the Examples.

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